

Cellular structure in system of interacting particles.

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The general description of formation the cellular structure in the system of interacting particles is proposed. Interactions between particles are presumably well-understood and the phase transition in which can be studied in the scale of particle resolution. We presented analytical results of possible cellular structures for suspension of colloidal particles, in system particles immersed in liquid crystal and gravitational system. We have shown that cellular structure formation can occur in system of interacting particles for realistic values of temperature and particles concentration.

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At the same time the resulting physical properties in the system of interacting particles have been the subject of much active research. The phase separation and ordering of many particles system and their resulting properties excite curiosity as fundamental physics as large number of viable application. For description the behavior the many particles system with different character of interaction we must develop approach which taking into account a spatial nonhomogeneous distribution of particle i.e cluster formation or cellular structure and more ordering other structures. Basically, statistical description of many particles systems concern homogeneous states. The most interesting and pressing problem in condense matter physic is the study of phase transition with spatial nonhomogeneous distribution of particle- cluster formation. This structure was observed in usual colloids [1],[2] in the system particle which introduced in liquid crystal [3],[4], [5] and even in distribution galactic system [6]. As evident from this examples, formation cellular structures in the system of interacting particle have been large-scale demonstration for different physical situation. Cellular structure in system particle was dramatic change the properties of condense matter. Depending of the size of particle was observed the formation of both reversible and irreversible clustering. During the past decade, colloidal system have been used as model system to understand phenomena the two dimensional melting transition. In usual colloids was observed the crystal like ordering, was observed hexagonal crystal structure [7]. Experimentally, it is observed that the initial stage of the cellular structure originates from region with lowest local density of particles. In all case exist the elastic interaction leads to spatially inhomogeneous distribution of such particles with formation of regions of pure from particles. The energy interaction in system particle have different character and value. Minimum of free energy realizes cellular structure and leads to stabilization the regions of pure elastic media, and the particles themselves are placed at the boundaries of those regions. To describe the conditions of formation and properties of these particle structures, one should take into account both aspects of the particle interaction. At first we shall give representation of the general approach in the description of

behavior in system of cooperating particles. Let's show as in this system can be realized of a first order phase transition with creation of spatially non-uniform distribution of particles. The formation of different structures depends upon the initial concentration of particles. The observation of optimum cluster size has important consequences for the formation cellular structure. The system will try minimize the energy by breaking it apart, and out of many ways it can be done, the system chooses the nucleation and further formation of cellular structures.

We would like show an investigating phenomena that occurs in colloidal system the formation of colloidal voids and cluster structures. Theoretical investigation of colloidal system focused on thermodynamic treatment or on general arguments. The essential point which is neglected any at these arguments is that the colloidal particles are interacting via their direct forces and indirect interaction mediated by free energy of solvent phases. We propose a general description which include effect contains parameters whose relation to formation of different structures in the system of interacting particles. Basically it consider very know Landau approach for first order phase transition coupled to the colloidal contribution and combined with the direct interaction between the colloidal particles. An analysis of this general model can predict a rich scenario of solvent induced colloidal phase separation with formation of cluster and cellular structures.

The physical properties depend on the structure of on individual particle. However practical exist within spatial nonuniform distribution of particles, and so inter particles interactions will be also influence the physical behavior of the this distribution and also aggregation process by within the spatial distribution formed. Characteristic of aggregation effect very difficult, although there have been attempt to measure fractal dimensional form of distribution particles. The presentation and develop method for system of interacting particle, several interesting feature have become evident. The method must describe to observations on similar system with different nature of interaction between particles which formed systems. Based on general approach we can estimate formation cellular structure in different system.

First from all we consider system of not interacting

particles. Instead of investigate the nonuniform distribution of particle we describe possibility formation the cavity where not particles. Empty cavity or pore in distribution particle is very simple find and measurement. In the case contiguous distribution of particles with concentration c the size of pore can determine as distance to nearest particles. We consider formation only cavity of spherical form. The form of cavity not play principal role and other form of pore we take into account after more precise the all process formation the cavity. For determination of probability of formation the cavity without particle used the Saslaw approach [6] which can describe the distribution of galactic. The probability depended from distribution of nearest particles. For different point of space the probability $p(r)dr$ of disclose the particle on the distance between r and $r + dr$ is equal the probability nonoccurrence of particles in the area with size r which must multiply on the probability to find the particle on the distance r . This relation have the following mathematical form:

$$p(r)dr = \left\{ 1 - \int_0^r p(r')dr' \right\} 4\pi cr^2 dr \quad (1)$$

This equation can rewrite in equivalent form:

$$\frac{d}{dr} \left\{ \frac{p(r)}{4\pi cr^2} \right\} = -p(r) = - \left\{ \frac{p(r)}{4\pi cr^2} \right\} 4\pi cr^2 \quad (2)$$

which have solution

$$p(r) = 4\pi cr^2 \exp\left(-\frac{4\pi cr^2}{3}\right) \quad (3)$$

The probability $p(r)dr$ of disclose the particle on the distance between r and $r + dr$ is equal the probability nonoccurrence of particles in volume V multiply on the probability $c dV$ to find the particle in the volume between V and $V + dV$: $p(r)dr = cP dV$. From this relation as result we can obtain the probability disclose the cavity without particle with volume V in the form

$$P(V) = \exp(-cV) = \exp(-N) \quad (4)$$

for Poisson distribution. The main size of area without particle can estimate from relation $P(V) \simeq \frac{1}{2}$. Obvious, that in system of not interacting particle we can obtain only nonuniform distribution of particles, but we have non zero the probability disclose the cavity without particle with volume V .

Now, we can find analytical result for the probability disclose the cavity without particle with random selection the volume V in the case of system interacting particles. The probability the presence in system interaction particles in ground canonical assemble N particles in volume V at temperature T can be write in the standard form [10]:

$$W(N) = \exp\{\beta\mu N - \beta F\} \quad (5)$$

where $\beta = \frac{1}{kT}$ inverse temperature, μ chemical potential, and $F(N, V, T)$ is free energy which can calculate with

the help of canonical assemble. With this probability to find the mean value of derived magnitude $\exp(qN)$ which must depend from number of particles

$$\begin{aligned} \langle \exp(qN) \rangle &= \sum_N \exp(qN) W(N) = \\ G^{-1} \sum_N \exp\{(\beta\mu + q)N - \beta F\} \\ &\equiv \exp\{\Psi(\beta\mu + q) - \Psi(\beta\mu)\} \end{aligned} \quad (6)$$

where we used the very know relation between statistical sums of ground canonical assemble G and thermodynamic function:

$$\ln G(\mu, V, T) = \frac{PV}{kT} \equiv \Psi(\mu, V, T) \quad (7)$$

The previous relation can rewrite in other form:

$$\begin{aligned} \sum_N z^N W(N) &= \exp\{\Psi(z \exp(\beta\mu)) - \Psi(\exp(\beta\mu))\} = \\ \exp(-\Psi) \exp(\Psi(z \exp(\beta\mu))) \end{aligned} \quad (8)$$

Now we can expansion in series at z the right part this relation and to compare the equal power of z in both part equation we obtain

$$W(N) = \exp(-\Psi) \frac{\exp(\beta\mu)}{N!} (\exp \Psi)_0^N \quad (9)$$

where

$$(\exp \Psi)_0^N = \left[\left(\frac{d}{d(\exp(\beta\mu))} \right)^N \exp \Psi(\exp(\beta\mu)) \right] \quad (10)$$

when $\exp(\beta\mu) = 0$. After this operation we can obtain the probability find the empty cavity in distribution of interacting particles. This probability can write in the form:

$$W(0) = \exp\left(-\frac{PV}{kT}\right) \quad (11)$$

If we know the equation of states we can estimate in general case the probability existence the cavity without particle in the case of system interacting particles. This relation show that existence the cavity without particle depend from equation of states for particles which filled in this cavity. In the case nonoccurrence of interaction in system we have the previous result of Poisson distribution. It is very good representative formula. If we remember that the Laplace pressure of bubble is $P = \frac{2\sigma}{R}$, where R is the radius of void bubble, we can obtain the probability in the very know form

$$W(0) = \exp\left(-\frac{8\pi\sigma R^2}{3kT}\right) \quad (12)$$

This is the probability formation the bubble on new phase under first order phase transition. In general case it is the bubble of void. It is very good representation of

argument to correct description the formation cavity of void.

First from all we consider the thermodynamic properties of systems weak interacting particle. In general case we can present the equation of state in the form

$$\frac{PV}{kT} = N(1 - b) \quad (13)$$

where b is the virial coefficient. The equation of state of the hard spheres gas can write as follows too:

$$PV = kTN \frac{1 + \nu + \nu^2 - \nu^3}{(1 - \nu)^3} \quad (14)$$

where $\nu = \frac{NV_0}{V}$ is packing factor a particle volume is excluded, has quite different form though asymptotically is similar to above ones. In the case of system particles which interact through short range repulsive as hard sphere and gravitation attractive on the far distance, in the limit of low packing factor, equation of state can write in the form :

$$PV = kTN + \frac{1}{2}N^2 \left(Uv - \frac{W_G v^{\frac{1}{3}}}{2N^{\frac{1}{3}}} \right). \quad (15)$$

All equations is like a Van der Waals equations of state with the second part of this equation representing the interaction in the system. If we have equations of state can obtain the probability existence the cavity without particle in the case of system interacting particles. Mean value of size the void or cavity without particle we can estimate compare probability to $\frac{1}{2}$. In the case noninteracting particle we can obtain $cV = \ln 2$ or number of particle which can put up to this void is $N = \ln 2 < 1$. In the system of noninteracting particles can not form the voids or cavity without particles. If we consider the system weak interaction particles we can use the equation of states in the standard form. In this case we can estimate the volume of void from relation

$$\frac{PV}{kT} = N(1 - b) = \ln 2. \quad (16)$$

as $(\frac{NV_0}{V}) \frac{V}{V_0} (1 - b) = \ln 2$

$$V = V_0 \frac{\ln 2}{\nu(1 - b)} \quad (17)$$

where V_0 is volume of one particles, and ν as previous is packing factor. If $\nu \sim 1$ and $b \ll 1$ is very small we can tell that in the system with weak interaction can not formed the voids. The size of voids will be the smallest as size of particles. If the packing factor decrease and increase the energy interaction between particle to come into the picture the condition to formation the cavity without particle and the size of one cavity can evaluation as

$$V = V_0 \frac{\ln 2}{\nu(1 - b)} \quad (18)$$

As example, if $\nu \sim 0,5b$ or smallest and $b = 0,5$ we obtain that $V \sim 3V_0$ or bigger. Next example is the hard spheres gas. In this case of system particles which interact through short range repulsive as hard sphere we can obtain that

$$V = V_0 \frac{\ln 2(1 - \nu)^3}{\nu(1 + \nu + \nu^2 - \nu^3)} \quad (19)$$

If $\nu \rightarrow 1$ we have that $V \rightarrow 0$. It is case compact packing hard sphere is obvious that in this system can not formed the voids. If $\nu \rightarrow 0$ as result we have that $V = V_0 \frac{\ln 2}{\nu}$ as previous result. We can assert that the formation of voids in the system of particles is result of interaction and depend from concentration of particles. In the case increasing of interaction of particles, when the relation between potential and kinetic energy is bigger and we can not use the description of the system in the term virial expansion we must used only equation of state.

In process of aggregation can produce few cellular. We can estimate the number of cell in general case. If in process of aggregation make up m cell in the volume \bar{V} which present the volume of pattern must hold the next relation:

$$mV + NV_0 = \bar{V}. \quad (20)$$

From this equation can obtain that

$$m = \frac{\bar{V}}{V} + N \frac{V_0}{V} \quad (21)$$

If use the previous relation between V and V_0 can obtain the number of cell as

$$m = N \frac{1 - b_2}{\ln 2} (1 - \nu) \quad (22)$$

From this equation we can conclude, that the number of cell without particles increase if decrease the packing factor ν and decrease the interaction energy. If packing factor $\eta \rightarrow 1$ that relation with crystal structures the number of voids go to zero. If we consider the system non interacting particle $b_2 \rightarrow 0$ we obtain that $m = N \frac{1}{\ln 2} (1 - \nu)$ and depended only packing factor. If $\nu \rightarrow 1$ the number of cell came to zero too. The number of particles in this case came to zero. If $\eta \rightarrow 1$ the number of cellular came to zero on other motivation. In this case all particles formed close packing system and in this system can not formed the cavity without particles.

If we have the inter particle interaction energy, we can study the thermodynamic behavior of an aggregate of such particles and describe the condition for the creation of new structure. The character and intensity of the inter particle interaction in the system of particles in different matter can be such that a temperature and concentration phase transition and produce a spatially inhomogeneous distribution the particles in the investigating system [8] [9]. We must describe the first-order phase transition when the external field present surface boundary condition on

all particles. In order to demonstrate the mechanism and character of the phase transition accompanied by the formation of the inhomogeneous distribution of the system foreign spherical particles. For this case the free energy of particles in the self-consistent field approach and the many-body approximation can be written in the form:

$$F = F_p + F_s + F(n) \quad (23)$$

where the first part

$$F_p = \int U(\vec{r} - \vec{r}') f(\vec{r}) f(\vec{r}') d\vec{r} d\vec{r}' + \dots \quad (24)$$

describe the free energy which cam from interaction in term function $f(\vec{r})$ spatially distribution particles. The simplest free energy including a interaction terms that respect this local gauge symmetry. Se second part

$$F_s = \int \{f(\vec{r}) \ln f(\vec{r}) + [1 - f(\vec{r})] \ln[1 - f(\vec{r})] d\vec{r} \quad (25)$$

is the entropy part free energy. This kind the entropy part the free energy is motivation that the two classical particle not possible occupation own space place. Next, the free energy resulting from the coupling between distribution function and colloidal coordinates can modelled by

$$F_n = \int f(\vec{r}) \sum_i W(\vec{R}_i - \vec{r}) d\vec{r} \quad (26)$$

where $W(r)$ contains microscopical information about the wetting properties of the particles surface.

The minima of the free energy corresponds to the self-consistent field solution for $f(r)$. Each of thermodynamic functions of state corresponds to a solution that describes some phase of particle arrangement. If their distribution can be inhomogeneous, then the solution serves to find the stable phase associated with the interaction temperature and character. The minima of the free energy corresponds to the self-consistent field solution for $f(r)$. Each of thermodynamic functions of state corresponds to a solution that describes some phase of particle arrangement. If their distribution can be inhomogeneous, then the solution serves to find the stable phase associated with the interaction temperature and character. If the particle solution is disordered, then by definition the mean value $f(\vec{r}) = c$, where c is the relative particle concentration. The concentration inhomogeneity gives rise to an additional term $f(\vec{r}) = c \pm \varphi(\vec{r})$ where $\varphi(\vec{r})$ is the change of the probability distribution function of the particles. If the concentration inhomogeneities are smooth and their scale is much longer the inter particle distance, the quantity may be interpreted as the change of particle composition. When passing from to continuum description, we can write the free energy increment, associated with the inhomogeneous particles distribution in the term of the power series expansion in using

the long-wavelength expansion of the concentration i.e. $\varphi(\vec{r}') = \varphi(\vec{r}) + \vec{\rho}_i \partial_i \varphi(\vec{r}) + \frac{1}{2} \vec{\rho}_i \vec{\rho}_j \partial_j \partial_i \varphi(\vec{r}) + \dots$. Where $\vec{\rho} = \vec{r} - \vec{r}'$ distance between two particles. In this case we may be rewrite the part free energy, which is dependence from the change of the probability distribution function of the particles in the form:

$$\Delta F(\varphi) = \int d\vec{r} \left\{ \frac{1}{2} l^2 (\nabla \varphi)^2 - \frac{1}{2} \mu^2 \varphi^2 + \frac{1}{4} \lambda \varphi^4 - \varepsilon \varphi \right\} \quad (27)$$

Where

$$\mu^2 \equiv \left(V - \frac{kT}{c(1-c)} \right), \quad V = \int U(\vec{\rho}) d\vec{\rho}, \quad (28)$$

and

$$l^2 = \int U(\vec{\rho}) \vec{\rho}^2 d\vec{\rho}, \quad (29)$$

λ is the coefficient responsible for nonlinearity of system, which is induced the many-body interaction in system particles. The coefficient $\varepsilon = N 4\pi R_0^2 W$ present the energy which include every particle through the wetting effect, where R_0 is size of particle and W present the anchoring energy of molecules of matter with surface of particle. This coefficient can introduce if we have the same wetting effect on every particle. In this case in general presentation the free energy not exist none even terms because the distribution function of particles satisfy the relation: $\int f(\vec{r}) d\vec{r} = N$, $\int \varphi(\vec{r}) d\vec{r} = 0$. The expression is the Landau free energy of a system particles which foreign in matter, below the phase transition temperature of this system. Thus we see that the minimum of the functional realizes a spatially inhomogeneous macro particle distribution only provided the sing satisfy some relation and the values of coefficients determined by the inter particle interaction. In order to reveal the condition under which the homogeneous particles distribution become unstable, we have to calculate all the coefficient. Temperature of the phase transition to new states the inhomogeneous distribution of particles may be determined from following relation

$$kT_c = c(1-c)V \quad (30)$$

The functional (23) is very well know functional, which description the first -order phase transition with accompanied the cluster formation in the system of the interacting particles. The most important contribution in the concentration is associated with the field configuration for which the value of the free energy is minimum, i.e.:

$$\Delta \varphi - \frac{dV}{d\varphi} = 0 \quad (31)$$

Where

$$V = -\frac{1}{2} \mu^2 \varphi^2 + \frac{1}{4} \lambda \varphi^4 - \varepsilon \varphi \quad (32)$$

can be used as potential energy in our case. Substitution the solution in the expression from the free energy yield and its variation due to the formation of new phase. In the case when the difference of minimum effective potential values is greater than the barrier height, the solution in our case the free energy one cluster is described by the expression :

$$\begin{aligned}\Delta F &= 4\pi \int_0^\infty r^2 dr \left\{ \frac{1}{2} \left(\frac{d\varphi}{dr} \right)^2 + V(\varphi) \right\} \\ &= -\frac{4\pi}{3} r^3 \varepsilon + 4\pi r^2 \sigma\end{aligned}\quad (33)$$

Where σ is the surface energy of the cluster boundary that is equal the free energy corresponding to the solution of the one-dimensional problem, i.e.

$$\sigma = \int_0^\infty dr \left\{ \frac{1}{2} \left(\frac{d\varphi}{dr} \right)^2 + V(\varphi) \right\} = \int_0^\infty d\varphi \sqrt{2V(\varphi)} \quad (34)$$

The radius of the new phase cluster by the minimum of the free energy. It is given by $\tilde{R}_0 = \frac{2\sigma}{\varepsilon}$. As is very know we can obtain $\varepsilon = \frac{2\mu\epsilon}{\lambda^{\frac{1}{2}}}$ and $\sigma = \frac{\mu^3}{3\lambda}$, then $R = \frac{\mu^2 l}{3\lambda^{\frac{1}{2}} \varepsilon}$ in our case and the effective value of the free energy variation from cluster formation is given by

$$\Delta F = \frac{8\pi\sigma R^2}{3} \quad (35)$$

The probability of formation one cluster can write in the form:

$$P(\tilde{R}) = \exp\left(-\frac{\Delta F}{kT}\right) = \exp\left(-\frac{8\pi\sigma R^2}{3}\right) \quad (36)$$

They sometimes possess mixed physical properties of their elements, but in many cases quite new properties emerge, reflecting new structural organization of their elements. The characteristic dimensions of the spatially inhomogeneous distribution of the concentration of particles in the end, become a criterion the first order phase transition with cluster formation in the system particle. The criterion of instability given by this relation can be interpreted as a condition for formation of spatially non-uniform distribution at a given temperature, which depends on the concentration of particles and characteristic length of the new structure. If we have the some fixed concentration of particles in the system the process of aggregation finished when all particle to assemble in few cluster. The size of cluster will be growth to time when all particle will be located only cluster. Cluster formed the interaction energy and distribution the particle in one cluster can consider homogeneous. If the concentration is bigger the volume of cluster growth too, and come the moment when the particle formed one cluster which to hold a position on volume of all particles. Other volume will be formed the voids. If the concentration is small we will be observer only cluster with equilibrium size, if the concentration is bigger as $\nu > \frac{1}{2}$ we obtain the one cluster and few voids. In present approach we can estimate the size of voids as characteristic length of instability the nonuniform distribution of particle. In summary we have independently estimated the spontaneous formation loosely bound, order aggregates of colloidal particles and possible formation the cellular structures as result the different nature of interaction.

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